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Observation of coexistence of 1D and 2D nanostructures in cobalt dipyrromethene trimer complexes adsorbed on a graphite surface

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ABSTRACT

We report the direct observation of 1D and 2D nanostructures of cobalt dipyrromethene trimer complexes adsorbed on a highly oriented pyrolytic graphite surface using scanning tunneling microscopy (STM). STM images showed two types of ordered structures coexisting on the surface: long 1D molecular chains isolated on the terraces, and 2D hexagonal patterns confined by a 1D chain and/or a graphite step edge. These 1D and 2D structures are attributed to 'edge-on' and 'face-on' complex alignments on the surface, respectively. In both configurations, substrate-mediated molecule–molecule interactions may play a significant role in stabilizing the nanostructures.

The adsorption of functional molecules on solid surfaces is becoming an important aspect of nanotechnology [1]. Molecular electronics—the integration of functional molecules to make specific functionalities on an integrated circuit—is a promising approach to reducing device size. In the fabrication of functional structures and devices, porphyrins are important materials because their conjugated and highly delocalized π-bonds yield various unusual chemical and physical properties [2–4]. To date, the assembly method has been widely used to construct 2D and 3D molecular structures through specific molecule–molecule and molecule–substrate interactions, whereas the formation of 1D molecular structures has been less explored. One-dimensional templates, such as step edges on a surface, have frequently been proposed to form 1D molecular arrays.

The rigid-planar nature of porphyrins has advantages in the assembly of 2D nanostructures on solid surfaces [5]; however, the lack of conformational flexibility can also be limiting. Porphyrin complexes are held together by covalent bonds, but self-assembled porphyrin structures are held together by weaker interactions such as hydrogen bonding and metal coordination, affording very versatile systems. Recently, dipyrromethenes, which can form neutral complexes with various metal ions, have been introduced as flexible and versatile ligands in the area of supramolecular chemistry. For example, bisdipyrromethene metal complexes featuring double helical structures or triangular structures have been reported [6–8].

In the present study, we used scanning tunneling microscopy (STM) to examine the nanostructures formed by cobalt dipyrromethene trimer (CDT) complexes adsorbed on a highly ordered pyrolytic graphite (HOPG) surface. We observed long 1D molecular chains isolated on terraces coexisting with 2D hexagonal patterns, features that are not observed in porphyrin-based nanostructures. Based on the heights of the STM topography, we conclude that the 1D molecular chains are comprised of complexes with an 'edge-on' alignment whereas the 2D hexagonal patterns are made up of complexes with a 'face-on' alignment on the graphite surface.

The CDT complex shown in Fig. 1 was prepared in the University of British Colombia [6–8]. The structure and purity of the compound were confirmed by ^{1}H nuclear magnetic resonance spectroscopy. The complex is composed of three cobalt dipyrromethene monomers surrounding a cavity in the middle. It was possible to obtain single crystals of this trimer suitable for X-ray diffraction analysis. Molecular modeling predicts an outer diameter of the trimer of 2.6 nm and a height of 2.1 nm. For adsorption of the CDT complexes onto a graphite surface (Advanced Ceramics, grade ZYA), the complex was first dissolved in dichloromethane at a concentration on the order of 1.0×10^{-5} M. Dichloromethane was chosen as the solvent because it can be removed from the surface under the conditions used. A droplet of the solution was applied onto a freshly cleaved surface and left to dry in air either at room temperature or at 100 °C for several hours. The droplet spread evenly over the surface, resulting

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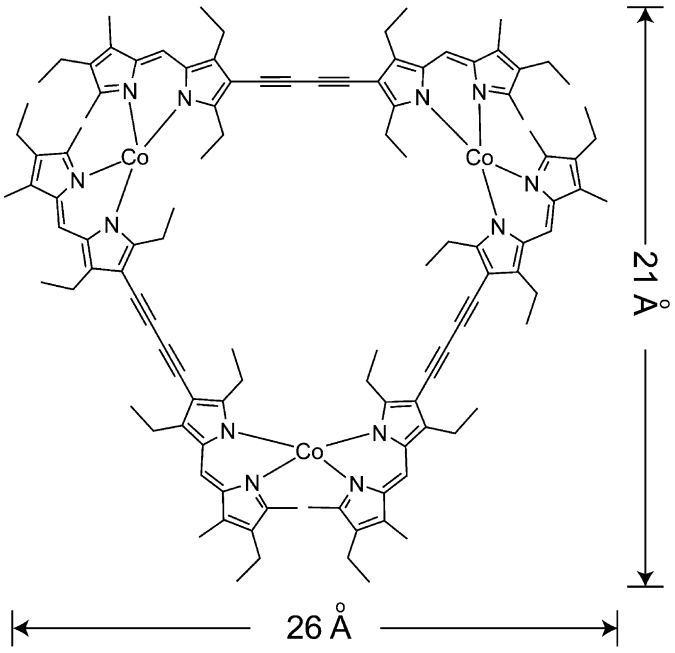

Fig. 1. Molecular structure of a cobalt dipyrromethene trimer complex with dimensions indicated.

in uniform coverage of the entire surface with CDT. All solvent appeared to have evaporated within a few minutes, leaving behind adsorbed CDT complexes. We expect that heating at 100 °C would remove any residual solvent molecules trapped in the CDT nanostructures on the surface.

STM images were obtained using a commercial scanning tunneling microscope (NT-MDT and NanoSurf) under ambient conditions [9]. STM tips were mechanically cut from a 0.25 mm Pt/Ir wire. Constant current mode (topographical imaging) was employed to investigate the static properties of the structures. All of the images shown are raw data with mean plane subtraction to reduce the thermal drift effect. The features of the adsorbed CDT complexes appear the same on the substrates evaporated at room temperature and 100 °C, indicating that the morphology of the sample evaporated at room temperature is not influenced by any residual solvent molecules that may have remained. The concentration and volume of the solution used in the experiment were carefully chosen to ensure that the amount of CDT adsorbed on the graphite surface was sufficient to take STM images.

STM imaging revealed two types of CDT molecular assemblies coexisting on the same graphite surface, as shown in Figs. 2 and 3. These molecular arrangements were observed by repeated scanning under very mild tunneling conditions. 1D chains of the type shown in Fig. 2(a) were found to have lengths extending up to a few hundred nanometers (not shown). At room temperature, where thermal mobility is appreciable, well-ordered and isolated chains were observed on the terraces of the surface; this finding indicates that there are significant adsorbate–substrate interactions in this system.

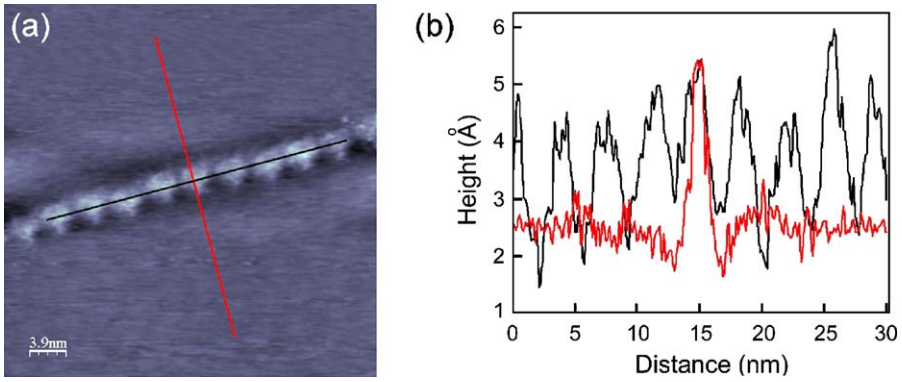

Fig. 2. (a) STM topographical image showing a 1D molecular chain structure of cobalt dipyrromethene trimer complexes adsorbed on a graphite surface and (b) cross-sectional cuts taken along the chain (black) and along the direction perpendicular to the chain (red). The image was obtained at a sample bias voltage of 200 mV and a tunneling current of 45 pA. Thermal drift was not compensated for in the STM image. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

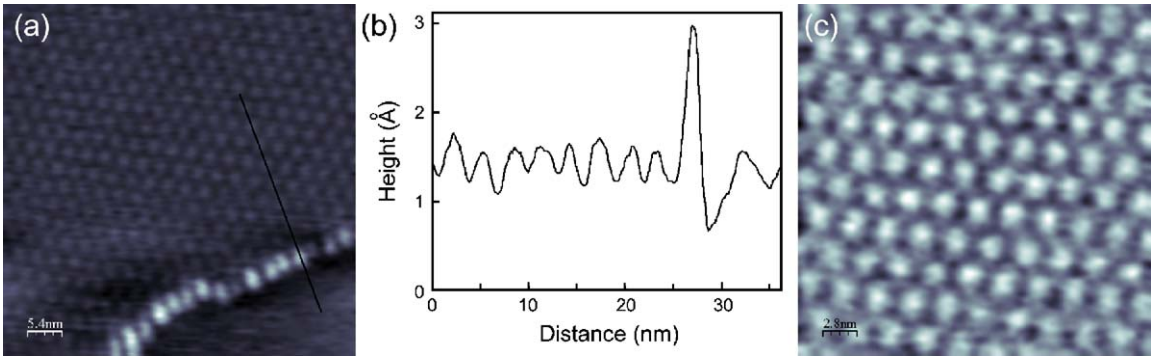

Fig. 3. (a) STM topographical image showing both a 1D chain and a 2D hexagonal pattern of cobalt dipyrromethene trimer complexes adsorbed on a graphite surface and (b) a cross-sectional cut taken across the structures. (c) Magnified STM topographical image of the hexagonal pattern. The images were obtained at a sample bias voltage of 200 mV and a tunneling current of 100 pA. Thermal drift was not compensated for in the STM image.